

Mass Spectra of Fluorocarbons*

Fred L. Mohler, Vernon H. Dibeler, and R. M. Reese

Mass spectra of 22 fluorocarbons have been measured on a 180° Consolidated mass spectrometer, and the results are presented in six tables of spectral data. These include seven normal paraffins from methane to heptane; isopentane and isohexane; three pure cyclics and methylcyclohexane; four olefins; three C_4F_6 isomers; a dicyclic; and a tricyclic. These spectra are very different from the hydrocarbon analogs. In all the paraffins the most abundant ion is CF_2^+ , and the molecule ions are very small or absent. Spectra of the unsaturated compounds and the cyclics are more distinctive than the normal paraffins. In the paraffins, ions of formula C_nF_{2n+1} tend to be largest, except that when one carbon is removed the largest ion is C_nF_{2n-1} . In cyclics, C_nF_{2n-1} ions tend to be largest; in the dicyclic, C_nF_{2n-3} ions are largest; and in the tricyclic, C_nF_{2n-5} ions tend to be largest. The tricyclic C_8F_{12} is probably a fused cyclobutane structure. The dicyclic is completely fluorinated methylnaphthalene, $C_{11}F_{20}$, and is the heaviest compound ever run on the Bureau's mass spectrometer. In the perfluoroparaffins there is a progressive increase in the current per unit pressure for the CF_2^+ ion with increasing molecular weight of the fluorocarbon. In incompletely fluorinated molecules containing an H atom the larger ion peaks containing H will correspond with the larger peaks in the perfluoro spectrum, with H substituted for a fluorine atom.

1. Introduction

The growing interest in fluorocarbon chemistry and technology makes it worth while to obtain mass spectra of perfluorohydrocarbons as a basis for chemical analysis of unknown mixtures of fluorocarbons. Also, it is of theoretical interest to see how these spectra differ from the hydrocarbon mass spectra. The Mass Spectrometry Section of the National Bureau of Standards has for several years been collecting mass spectra of fluorocarbons as compounds become available, and the present paper gives a compilation of spectra obtained to date. A previous paper [1]¹ includes data on five perfluorohydrocarbons. The present summary includes these compounds. Other laboratories have obtained mass spectra of a variety of fluorinated hydrocarbons, but no systematic compilation of spectra has been published.

Complete spectra of all the fluorocarbons included in this paper have been published in the API Catalog of Mass Spectral Data [2]. When the mass spectrum of a fluorocarbon is tabulated in the conventional manner in the order of increasing molecular weight of the ions, ions with different numbers of carbon atoms and of fluorine atoms become mixed in a confusing disorder. For that reason, spectra are presented here in order of the number of carbon atoms and the number of fluorine atoms in each ion. This is convenient for the purpose of interpreting the spectra in terms of molecular structure and for comparison with hydrocarbon spectra. For purposes of chemical analysis the conventional tables are, of course, preferable.

2. Experimental Details

Most of the mass spectra were obtained with a type 103 Consolidated mass spectrometer equipped with a micromanometer [3] to measure the pressure in the

inlet reservoir. An ionizing voltage of 70 volts was used, and the metastable ions were suppressed. For the heavier compounds the suppressor voltage was adjusted to give a resolving power of about 350. The temperature of the ionization chamber was 250° C. The heaviest compounds require a magnetic field in excess of the rated capacity of the magnet, but there was no evidence of overheating in the time required to scan the spectrum. Some of the mass spectra were obtained with a type 102 mass spectrometer before the type 103 instrument was installed. There are only minor differences in spectra obtained with the two types of instrument.

We are indebted to Dr. George H. Cady, University of Washington; The M. W. Kellogg Co.; Minnesota Mining & Manufacturing Co.; the Jackson Laboratories of the E. I. du Pont de Nemours Co., Inc.; and to others acknowledged later for making available the various fluorocarbons. Most of these compounds are available only in small experimental batches. The purity was in all cases adequate for a reliable description of the spectra. Trace amounts of molecules containing one H or one Cl atom were sometimes found, but, except where noted, there was no evidence of heavier fluorocarbons as impurities. The API tables include mass peaks as small as 0.01 percent of the maximum peak. For brevity, we omit many of the small peaks in the tables to give a concise presentation of the major features.

There are no difficulties in running fluorocarbons in the mass spectrometer, although special precautions were taken in handling the *iso*- C_4F_6 , because of the reported toxicity of this compound [7]. The vapor pressures are high and are of the order of magnitude of the vapor pressures of the hydrogen analogs. They are inert and are not strongly adsorbed, so they are quickly pumped out, with no serious memory effects in spite of the high molecular weight.

3. Results

Table 1 lists the larger ion peaks in the mass spectra of normal perfluoroparaffins from methane to *n*-

*This paper was presented at the Pittsburgh Conference on Analytical Chemistry and Spectrochemistry, in March 1952.

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Mass spectra of normal perfluoroparaffins

Ion	CF ₄	C ₂ F ₆	C ₃ F ₈	C ₄ F ₁₀	C ₅ F ₁₂	C ₆ F ₁₄	C ₇ F ₁₆
C.....	7.8	1.49	2.4	0.19	0.05	0.25	0.03
F.....	6.7	1.22	0.98	.14	.08	.23	.05
CF.....	4.9	18.3	28.8	12.2	9.2	11.3	6.08
CF ₂	11.8	10.1	9.3	4.16	3.12	2.50	1.86
CF ₃	100	100	100	100	100	100	100
CF ₄	0	-----	-----	-----	-----	-----	-----
C ₂ F ₅	-----	0.55	6.55	8.40	7.2	13.2	7.34
C ₃ F ₇	-----	41.3	9.0	18.3	29.5	27.8	27.0
C ₄ F ₉	-----	0.15	-----	-----	-----	-----	-----
C ₅ F ₁₁	-----	-----	0.55	1.20	2.06	4.24	2.38
C ₆ F ₁₃	-----	-----	.23	8.37	6.54	13.9	13.3
C ₇ F ₁₅	-----	-----	.05	2.55	1.10	1.96	.88
C ₈ F ₁₇	-----	-----	24.6	2.14	9.73	18.9	20.5
C ₉ F ₁₉	-----	-----	0	-----	-----	-----	-----
C ₄ F ₇	-----	-----	-----	0.03	3.25	2.36	2.53
C ₅ F ₉	-----	-----	-----	2.57	0.27	3.96	8.48
C ₆ F ₁₁	-----	-----	-----	0	-----	-----	-----
C ₇ F ₁₃	-----	-----	-----	-----	0	2.67	0.80
C ₈ F ₁₅	-----	-----	-----	-----	0.77	0.08	1.20
C ₉ F ₁₇	-----	-----	-----	-----	.03	-----	-----
C ₁₀ F ₁₉	-----	-----	-----	-----	-----	-----	1.08
C ₁₁ F ₂₁	-----	-----	-----	-----	-----	1.11	0.02
C ₁₂ F ₂₃	-----	-----	-----	-----	-----	0.05	-----
C ₁₃ F ₂₅	-----	-----	-----	-----	-----	-----	.09
C ₁₄ F ₂₇	-----	-----	-----	-----	-----	-----	0
Relative sensitivity.....	0.57	0.97	1.71	1.82	2.59	2.65	3.42

heptane. Ions are listed in the order of the number of carbon atoms and the number of fluorine atoms in each ion, and intensities are relative to CF₃⁺ taken as 100. The last row gives the sensitivity (current per unit pressure) for the CF₃⁺ ion relative to the sensitivity of normal butane at mass 43.

In each of these spectra by far the largest peak is CF₃⁺, and the molecule ion peak is very small or zero. In each group of peaks containing *n* carbon atoms the maximum peak is C_{*n*}F_{2*n*+1}, except that for molecules heavier than propane, when one carbon atom is removed from the molecule the maximum peak is C_{*n*}F_{2*n*-1}. Thus in C₆F₁₄ the largest peak containing five carbon atoms is C₅F₁₃⁺. In C₇F₁₆ the largest peak containing six carbon atoms is C₆F₁₅⁺, but the largest peak with five carbon atoms is C₅F₁₃⁺. The size of these maximum peaks decreases progressively with increasing molecular weight, and the spectra of the heavier compounds are very similar except near the heavy end, and these distinctive peaks are small. In normal hydrocarbon paraffins the maximum peaks are also C_{*n*}H_{2*n*+1}, except that the molecule ion peak is larger. The largest of these peaks is C₃H₇ or C₄H₉.

In these fluorocarbons the sensitivity for the CF₃⁺ ion progressively increases with increasing molecular weight. The total ionization (the sum of the mass peaks times the sensitivity) increases at much the same rate.

Doubly charged ions are observed as follows: In CF₄ the intensities of CF₂²⁺ and of CF₃²⁺ are 3.9 and 1.25, respectively, relative to CF₃⁺; in C₃F₈ the intensity of C₃F₈²⁺ is 0.28, and in C₅F₁₂ the ion C₅F₁₂²⁺ is 0.09. Thus, molecules of formula C_{*n*}F_{2*n*+2} give ions C_{*n*}F_{*n*+1}²⁺, and in molecules where *n* is an even number a singly charged ion will mask the doubly charged ion. In spectra obtained with the

type 102 mass spectrometer some metastable transition peaks were observed, but they were very small [1].

There are only two examples of branched fluorocarbons, perfluoroisopentane and isohexane. Table 2 shows the spectra and, for comparison, the spectra of the normal compounds from table 1. The most conspicuous difference in both the pentanes and the hexanes is found in the relative intensities of the C₃F₇⁺ ion. It appears as if the isopropyl radical CF(CF₃)₂ did not contribute at all to this peak, and that the normal propyl ion CF₃-CF₂-CF₂⁺ accounted for the observed ion current. In isopentane, C₃F₇⁺ is nearly zero, and in *n*-pentane and isohexane, each of which contain one *n*-propyl radical, the relative intensity is about 9, whereas in *n*-hexane, which consists of two *n*-propyl radicals, the relative intensity is twice as great. C₂F₅⁺ is also roughly twice as great in the normal compounds containing two terminal ethyl radicals as in the iso-compounds containing one terminal ethyl radical.

Table 3 gives mass spectra of three pure cyclics and methylcyclohexane. The spectra are very distinctive with few common characteristics. The molecule ions are small, and, with two minor exceptions, the peaks C_{*n*}F_{2*n*-1} are the largest peaks for *n* greater than 2. In the pure cyclics, production of CF₃⁺ involves a rearrangement of atoms, but it is a large peak. The ion C₂F₅⁺ also involves a rearrangement of atoms in these compounds. No doubly charged ions are observed in these spectra.

Table 4 lists mass spectra of four perfluoroolefins. The spectra are distinctive, with no obvious common characteristics, except that the molecule ions are fairly large and CF⁺ is large. CF₃⁺ is small in C₂F₄, where a rearrangement of atoms is involved in the ionization process. The two butenes have very

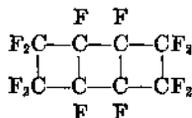
distinctive spectra, and both are different from the isomer cyclo-C₄F₈ given in table 3. The relative intensities of C₃F₅⁺, C₃F₄⁺, C₂F₄⁺, and CF₃⁺ are strikingly different in the three spectra. C₃F₈ gives a relatively large doubly charged ion peak C₃F₅²⁺ of intensity 2.17, and C₃F₇²⁺ has intensity 0.16. In 1-butene C₃F₅²⁺ of intensity 0.11 is observed.

Table 5 lists mass spectra of three C₄F₈ isomers: 1,3-Butadiene, CF₂=CF-CF=CF₂; cyclobutene, CF₂-CF=CF-CF₂; and 2-butyne, CF₃-C≡C-CF₃.

In these compounds C₃F₅⁺ is the maximum peak. The relative intensities of C₄F₆⁺, C₄F₅⁺, and CF₂⁺ are distinctively different in the three compounds.

Table 6 includes mass spectra of a dicyclic and a tricyclic fluorocarbon. The dicyclic compound is completely fluorinated 1-methylnaphthalene, C₁₁F₂₀, prepared by E. T. McBee of Purdue University. This compound of molecular weight 512 is the heaviest compound ever run on the Bureau's mass spectrometer. Two small peaks ascribed to C₁₂F₁₅⁺ and C₁₁F₂₁⁺ indicate that there is some heavier impurity present. The maximum peak of each carbon group has the formula C_nF_{2n-3} for *n* greater than 4. The ions C₂F₃⁺ and C₃F₇⁺ involve rearrangement in the ionization. There are also many small peaks not included in table 6 that come either from rearrangement or from impurities.

The C₈F₁₂ compound was furnished by W. T. Miller of Cornell University and was described by Prober and Miller in 1949 [4]. When hexafluorobutadiene is heated, one of the products is a saturated fluorocarbon of formula C₈F₁₂. It has a freezing point of 40° C and a boiling point of 80° C. They state that "preliminary X-ray diffraction studies are consistent with the (following) structure":



The mass spectrum of table 6 can also be described as consistent with this structure. While the ions CF₃⁺ and C₂F₃⁺ involve rearrangements in the ionization process, if this is the structure, other spectra show that rearrangements to give these ions are very common in fluorocarbon spectra. It is perhaps significant that C₂F₇⁺ is the largest C₂ ion, C₄F₉⁺ the largest C₄ ion, and C₆F₉⁺ is fairly large. The spectrum shows a very uniform distribution of intensity from CF⁺ to C₈F₁₁⁺. The largest peaks in each carbon group are C_nF_{2n-5} beyond *n*=4.

4. Conclusions

The fluorocarbons included in this investigation cover a wide variety of compounds, but, with the exception of the normal perfluoroparaffins, there are not enough compounds of any chemical class to permit broad generalizations. The normal perfluoroparaffins show a marked regularity in their spectra that is quite different from the regularities found in

the hydrocarbon analogs. CF₃⁺ is by far the most abundant ion and accounts for half or more of the total ionization. Another research [5] shows that the appearance potential of this ion is the same (14.3 to 14.4 ev) in C₂F₆, C₃F₈, C₄F₁₀, and C₆F₁₄. (The value given in the reference for C₄F₁₀ is not correct.) As production of CF₃⁺ is the predominant ionization process, it is significant that the sensitivity, or current, per unit pressure increases progressively with increasing molecular weight.

In the ionization process a valence electron is removed, and this weakens the ionized bond. There are two possibilities, (1) either the molecule dissociates at the point where it was initially ionized or (2) the electrons rearrange themselves before there is time for dissociation and the dissociation occurs at some other bond than at the point initially ionized. On the first hypothesis, the probability of producing CF₃⁺ should be the same for all normal compounds heavier than ethane, for in each case one of two terminal C-C bonds has to be ionized. (We have seen that the ionization potential remains the same.) This is not the case, and the progressive increase in the probability of ionization indicates that wherever the molecule is initially ionized there is a high probability of breaking a terminal C-C bond to give CF₃⁺. Large molecules with many valence bonds afford a larger target area than small molecules. Wallenstein, Wahrhaftig, and Eyring [6] have advanced this second hypothesis concerning the ionization process to explain the relative intensities in hydrocarbon mass spectra, but in hydrocarbons, radicals other than CH₃ are preferentially ionized.

It has been noted that in normal perfluoroparaffins ions of formula C_nF_{2n+1} give the largest peak in each carbon group, except that in fragment ions with one carbon removed from the molecule C_nF_{2n-1} is the largest peak. In hydrocarbons, C_nH_{2n+1} is the largest, with rare exceptions. In the cyclics the ions C_nF_{2n-1} tend to be the largest for *n* greater than 2. In the dicyclic, C₁₁F₂₀, the ions C_nF_{2n-3} are largest, and in the tricyclic, C₈F₁₂, ions of formula C_nF_{2n-5} tend to be largest. In this respect patterns of fluorocarbons are simpler than hydrocarbons. In hydrocarbons there is a close resemblance between patterns of the 1-olefin and the isomeric cyclic. There is no such resemblance between cyclo-C₄F₈ and perfluoro-1-butene.

Identification and analysis of mixtures of perfluoroparaffins will be difficult because of the almost complete absence of molecule ions and the low intensity of all the heavier ions in these spectra. Unsaturated molecules and cyclics have very distinctive spectra and possibilities of analysis will be favorable when spectra of more compounds become available.

As there are gaps of several mass units between fluorocarbon peaks, impurities other than fluorocarbons are usually conspicuous. A common trace impurity will be molecules that are not completely fluorinated and contain one or two H atoms. The previous paper on mass spectra of fluorocarbons [1] includes a spectrum of cyclo-C₅F₈H, and it is found

that large peaks containing an H atom correspond closely in relative intensity to large peaks in the cyclo-C₅F₁₀ spectrum, with H substituted for one of the F atoms. We have qualitative evidence based on hydrogen impurities rather than pure compounds that this is a quite general relation and also holds when 2 H atoms are substituted for 2 F atoms in a molecule. Thus, if a trace of H is present, peaks containing H will not be adjacent to the large fluorocarbon peaks but will be 18 mass units less than the large peaks. With traces of chlorine in the fluorocarbon the larger peaks containing Cl will be 16 and 18 mass units heavier than the larger fluorocarbon peaks.

When any HF or F₂ is formed in a reaction this reacts with glass to give SiF₄. The SiF₃⁺ ion of mass 85 is by far the largest peak in the SiF₄ spectrum, and this will be a common impurity peak.

5. References

- [1] F. L. Mohler, E. G. Bloom, J. H. Lengel, and C. E. Wise, Mass spectra of some cyclic and straight chain fluorocarbons, *J. Am. Chem. Soc.* **71**, 337 (1949).
- [2] Catalog of mass spectral data, API Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.
- [3] V. H. Dibeler and F. Cordero, *J. Research NBS* **46**, 1 (1951) RP2167.
- [4] M. Prober and W. T. Miller, Jr., *J. Am. Chem. Soc.* **71**, 598 (1949).
- [5] V. H. Dibeler, R. M. Reese, and F. L. Mohler, *Phys. Rev.* **87**, 213 (1952) abstract.
- [6] M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, AECU Report 1484.
- [7] W. H. Pearson, Minnesota Mining & Manufacturing Co., private communication.

WASHINGTON, September 8, 1952.